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SANDWICH TEXTURE AND ITS EFFECT ON THE ELECTROPHYSICAL PROPERTIES OF LANTHANUM BOROGERMANATE BASED GLASS CERAMICS

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It is established by means of x-ray diffraction and electron microscopy that in $La_2O_3 – B_2O_3 – GeO_2$ glasses a lanthanum germanate $La_2Ge_2O_7$ film texture up to 5 μm thick, under which forms needle-like texture of stillwellite-like $LaBGeO_5$ possessing pyroelectric properties is formed in the surface layer on contact between the glass and a corundum substrate or under a load during heat-treatment in a wide temperature range. The temperature dependences of the dielectric and pyroelectric properties of the samples with $La_2Ge_2O_7 – LaBGeO_5 – La_2Ge_2O_7$ sandwich structure and ground samples containing only a stillwellite-like phase are studied.

Key words: texture, stillwellite, lanthanum borogermanate glass, microstructure, oriented crystallization, ferroelectric, pyroelectric constant.

Lanthanum borogermanate glass ceramics based on $LaBGeO_5$ with stillwellite structure is a ferroelectric and is characterized by an appreciable pyroelectric constant — $\gamma \sim 3$ nC/(cm$^2 \cdot$ K) [1] (according to the data in [2] $\gamma \sim 7$ nC/(cm$^2 \cdot$ K)), which combined with a low dielectric constant ($\varepsilon \sim 11$) gives very high pyroelectric activity γ/ε. Crystalline and glassy $LaBGeO_5$ possesses high electric resistance (more than $10^8\ \Omega \cdot$ cm at temperature 500°C) and low dielectric losses ($\tan\delta \sim 0.001$) in the working temperature range from – 20 to + 500°C. The properties taken together make this a promising pyroelectric material. In addition, crystals with stillwellite structure are nonlinearly optical (the SHG signal about 30 units relative to α-quartz).

It is shown in [3 – 5] that pyroelectric material can be obtained by oriented crystallization of lanthanum borogermanate (LBG) glass. The texturing capability of glasses belonging to different systems depends on many factors: the composition of the glass taking account of sublimation losses of the components, the quality of the surface working of the samples, the temperature regimes of crystallization, and so forth [6]. The instability of the technological parameters sharply decreases the reproducibility of the microstructure and the physical properties of textured glass ceramic, which is also characteristic for the LBG system. An efficient technology of pyroelectric textures with properties comparable to those of single crystals should give initial glass with high quality, low defect density, and uniform growth of texture on large areas.

The initial stages of surface crystallization largely determine the quality of the volume texture obtained as a result of long heat treatments. Crystallization processes in LBG glasses have been studied repeatedly [3, 7 – 11], but the understanding of the ratio of the volume and surface crystallization of glass with composition close to $LaBGeO_5$ stoichiometry needs to be clarified. The present article reports the results of studies of isothermal crystallization of LBG glass in the surface layer as a function of the presence or absence of contact between the glass surface and a ceramic substrate and as a function of the effect of the initial stages of texture-formation on the electrophysical properties of the samples.

The scheme described in [3, 7] was used to obtain the glass crystal pyroelectric material $LaBGeO_5$. The components $La(OH)_3$, H_3BO_3, and GeO_2 were used to make glass with the stoichiometric composition $La_2O_3 \cdot B_2O_3 \cdot 2GeO_2$, taking account of the data on boron evaporation during the glassmaking. The mix was made using very pure and analytically-pure initial materials.

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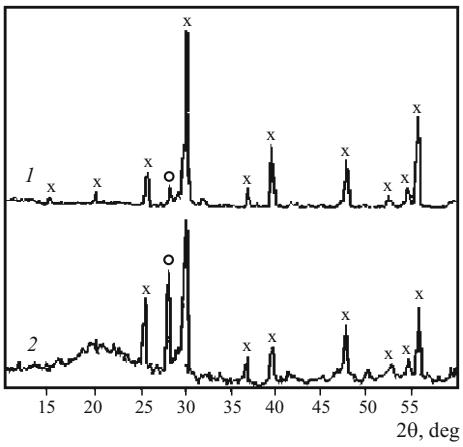

Fig. 1. X-ray diffraction patterns of a plate of LBG glass crystallized at temperature 980°C in 8 h: *1*, *2*) top (contact with air) and bottom (contact with a ceramic substrate), respectively, sides of the plate; ×) $LaBGeO_5$; ○) $La_2Ge_2O_5$.

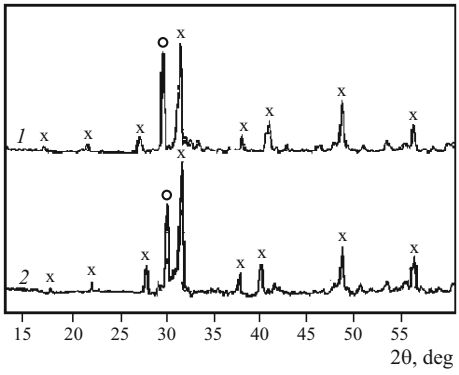

Fig. 2. X-ray diffraction patterns of a plate of LBG glass crystallized at temperature 980°C in 8 h "under pressure" 10 kPa with a ceramic plate placed on the crystallizing glass sample (both sides of the sample are in contact with a ceramic plate): *1*, *2*) top and bottom, respectively, sides of the plate; ×) $LaBGeO_5$; ○) $La_2Ge_2O_7$.

The glass was made at temperature 1300°C over 30 min in an electric furnace with silicon carbide heaters. The mix was heated at the rate about 10 K/min. The glass was poured onto a metal plate and pressed with another metal plate to thickness less than 0.8 mm. The plates were cut and about 1 cm^2 samples were obtained. The samples were polished on both sides to thickness 0.25 – 0.40 mm.

The polished glass plates were crystallized in a muffle furnace on a corundum substrate either in a free state or under a load: a corundum substrate with different mass (from 0 to 1 kg/cm^2) was placed on the glass plate. The crystallized samples were ground to thickness about 0.2 mm. Platinum electrodes were deposited on them; these electrodes were burned-in at temperature 700°C. The samples were polarized in a constant electric field 10 kV/mm at temperature 300°C in an atmosphere of compressed air under pressure 303 kPa

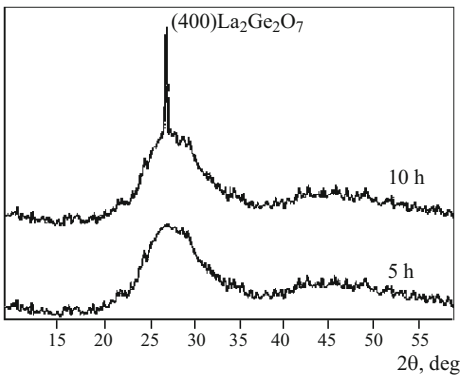

Fig. 3. X-ray diffraction pattern of LBG glass at the initial state of surface crystallization at temperature 685°C (the pattern was obtained from the surface of the sample).

over 45 min, after which the samples were cooled to room temperature in the presence of a field.

x-ray phase analysis of the surface of the glass crystalline plates and of finely comminuted powder was performed with a DRON-3M diffractometer using CuK_α radiation and a nickel filter. The measurements were performed at room temperature in the interval $2\theta = 10 - 60°$ with the detector moving at speeds ranging from 1/8 to 1 °/min. The crystalline phases were identified by comparing the relative intensities of the peaks of the crystalline reflections on the diffraction curve and the interplanar distances corresponding to them according to the data from the JCDFS (Joint Committee on Powder Diffraction Standards) electronic catalogue of diffraction patterns.

The microstructure of the samples and the morphological features of the surface were studied by electron microscopy with magnification × 3500 and × 10000.

The dielectric constant and the tangent of the angle of dielectric losses of the samples were investigated by dielectric spectroscopy on an automated facility using an NR 4284A (1V) bridge. The measurements were performed with ac current in the temperature interval 20 – 600°C and frequency range 50 Hz – 1 MHz. Samples in the form of parallelograms ($S\,[mm^2] \times d\,[mm] = 0.59 - 1.26 \times 0.27 - 0.40$) were used in the experiments. The blocking platinum electrodes were deposited on the smaller plane-parallel faces of the samples and burned-in at 800°C.

X-ray phase analysis of the crystallized plates of LBG glass (Fig. 1) established that the phase composition of the near-surface sections of the glass which do not come into contact with the ceramic (in the absence of a ceramic load) consists entirely of stillwellite $LaBGeO_5$. When glass – ceramic contact was established, the presence of a high-intensity Bragg reflection ($d = 3.17$ Å) was recorded in all cases and irrespective of the pressure on the sample (Fig. 2); this reflection is absent in the x-ray diffraction pattern of stillwellite but corresponds very well with the 100% line of the $La_2Ge_2O_7$ phase (Fig. 3).

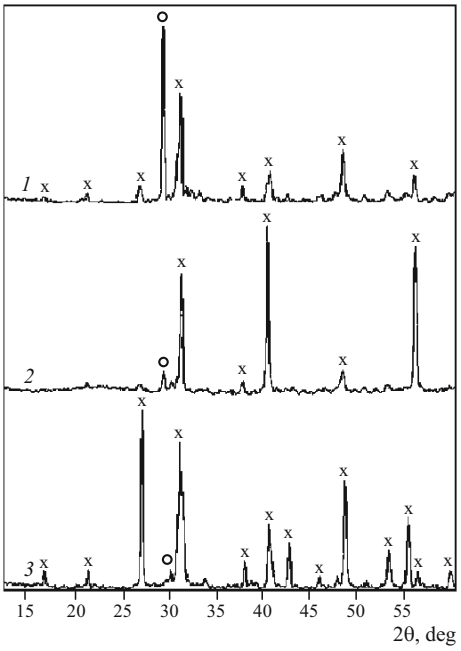

Fig. 4. X-ray diffraction patterns of a plate of LBG glass crystallized at 980°C in 8 h under a load in the form of a ceramic plate: *1*) initial plate; *2*) plate after grinding (40 μm thick layer removed); *3*) powder obtained by comminution of the crystallized glass; ×) $LaBGeO_5$; ○) $La_2Ge_2O_7$.

Figure 4 displays the x-ray diffraction patterns of a plate of LBG glass crystallized at temperature 980°C. It is evident that after grinding removes a 4 μm thick layer the 100% peak of the $La_2Ge_2O_7$ phase vanishes almost completely and the $LaBGeO_5$ texture dominates. Since no other reflections of the $La_2Ge_2O_7$ phase are observed in the x-ray diffraction pattern, it can be supposed that texture consisting of a $La_2Ge_2O_7$ film with maximum thickness about 5 μm forms on the surface of the LBG glass in a wide temperature range. This supposition is confirmed by the fact that no peaks due to $La_2Ge_2O_7$ were observed in the x-ray diffraction pattern of powder obtained by comminution of a crystallized plate (see Fig. 4). Thus, $LaBGeO_5$ is the main crystalline phase in the volume of the plate. It should be noted that in the case where the glass comes into contact with a ceramic substrate lanthanum germanate in the form of a thin film forms on the surface of LBG glass initially.

The presence of layered texture of crystallized LBG glass is also confirmed by electronic microscopy (Fig. 5). Taking account of the x-ray diffraction data, it can be supposed that the thin surface layer (see Fig. 3) is $La_2Ge_2O_7$ texture, while the needle-like $LaBGeO_5$ texture completely fills the volume of the sample. The content of the residual glass phase is low 10%; this is indicated by the absence of diffuse scattering of an amorphous nature in the x-ray diffraction pattern of LBG powder (see Fig. 4).

In summary, when LBG glass crystallizes, a sandwich structure consisting of a strongly textured, several microns thick, lanthanum germanate film on the surface of glass and a needle-like stillwellite texture which penetrates through the entire volume of the sample forms in the volume of the glass. The nature of the appearance of the film texture accompanying the appearance of glass – ceramic contact requires addition investigation, since no simple correlations between the parameters of the corundum lattice and $La_2Ge_2O_5$ are observed.

The two-texture surface microstructure which forms on crystallization of LBG glass is not unique. Recently, a phenomenon which is just as interesting was observed in [12], where the formation of two textures — fresnoite and benitoite — with the crystallization of glass with the composition (molar content, %) 30 BaO, 15 TiO_2, and 55 GeO_2 was observed.

An entire series of Bragg reflections of lanthanum germanate is observed with prolonged heat-treatments in the temperature range of bulk crystallization of glass (900 – 1000°C). This proves that lanthanum germanate is present even at the initial stages of crystallization (see Figs. 3 and 5).

Measurements of the temperature dependences of the dielectric properties of crystallized plates of LBG glass showed the presence of $La_2Ge_2O_7$ film texture has practically no effect on the value of ε and increases tan δ somewhat (Fig. 6). In all probability the latter effect is due to the high electric conductivity of $La_2Ge_2O_7$ as compared with stillwellite. For the same reason the pyroelectric constant of the textures, polarized under a field 10 kV/mm, before and after the removal of the lanthanum germanate layer remains practically unchanged (breakdown was not observed in the

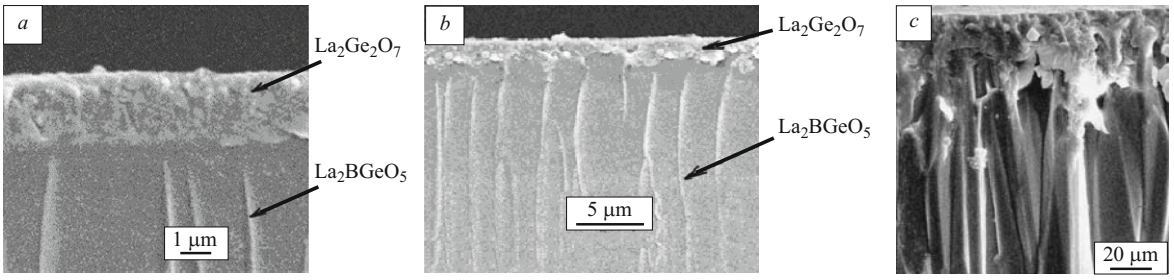

Fig. 5. Electron microscopic photographs of LBG glass: *a*, *b*) crystallization at 685°C in 10 h; *c*) crystallization at 980°C in 8 h.

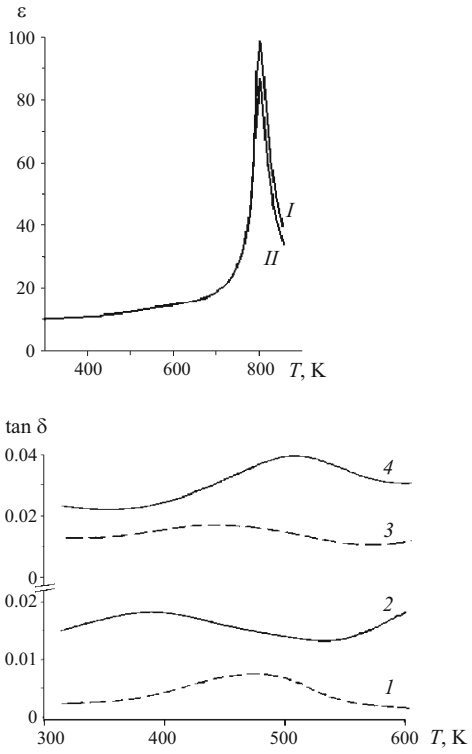

Fig. 6. Temperature dependence of ε and tan δ of the glass crystal texture of LBG glass (crystallization at temperature 980°C in 8 h) before (*I*, *1*, *2*) and after (*II*, *3*, *4*) mechanical removal of the $La_2Ge_2O_7$ layer.

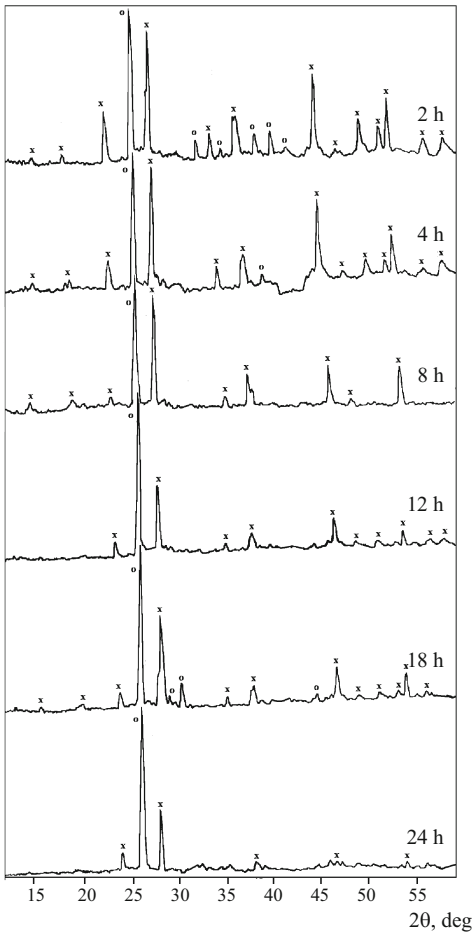

Fig. 7. X-ray diffraction patterns of LBG glass, crystallized at temperature 980°C over different times: ×) $LaBGeO_5$; ○) $La_2Ge_2O_7$.

samples with sandwich texture, even under a 15 kV/mm field). In the best samples γ reaches 3 nC/(cm^2 · K). Consequently, the presence of sandwich texture can be regarded as a positive factor in the technology of pyroelectric LBG materials, since a $La_2Ge_2O_7$ film makes it possible to polarize the plates using fields up to 10 kV/mm and higher.

Figure 7 illustrates well the relation between the $LaBGe_2O_5$ and $La_2Ge_2O_7$ phases precipitating from the glass. Evidently, depending on the heat-treatment, the quality of the textures improves, probably as a result of increased perfection of the crystals.

A thin layer of $La_2Ge_2O_7$ texture forms after soaking for 8 h. This layer coexists with a textured stillwellite-like phase $LaBGeO_5$. At subsequent stages of heat treatment, together with $La_2Ge_2O_7$ texture systematic degradation of the stillwellite-like phase $LaBGeO_5$ is observed. This can be attributed exclusively to the build-up of the $La_2Ge_2O_7$ layer. The x-ray absorption of this phase is very high (a 5 μm thick layer attenuates the primary beam by approximately a factor of 3), and a pattern of Bragg reflections is formed at a depth no greater than 10 μm.

This is confirmed well by the x-ray diffraction patterns of crystallized LBG glass before and after an about 10 μm thick surface layer is ground off the sample (Fig. 8). The stillwellite crystals grow through the entire depth of the glass, forming a uniform crystalline texture (Fig. 9).

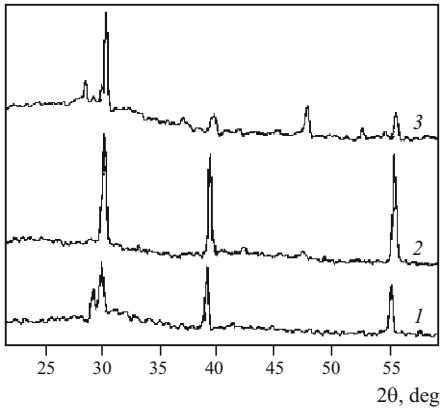

Fig. 8. X-ray diffraction patterns of a 1 mm thick layer-wise-ground LBG glass plate (crystallization at temperature 980°C in 8 h) after 0.10 mm (*1*), 0.17 mm (*2*), and 0.30 mm (*3*) have been are ground off.

In summary, adherence to the conditions for making glass and the technology of nucleation and formation of crystals makes it possible to obtain high-quality textured materi-

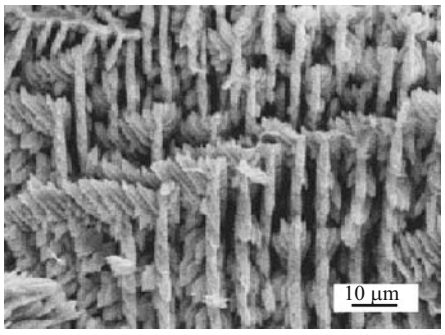

Fig. 9. Photomicrographs of the characteristic texture of LBG glass crystallized at temperature 980°C in 8 h.

als, whose pyroelectric properties are comparable to those of single-crystal $LaBGeO_5$.

REFERENCES

1. E. V. Milov and B. A. Strukov, "Pyroelectric effect and spontaneous polarization in high-temperature ferroelectric $LaBGeO_5$ (LBGO)," *Fiz. Tverd. Tela,* **43**, 495 – 498 (2001).
2. S. Yu. Stefanovich, B. V. Mill', and A. V. Butashin, "Ferroelectric phase transitions in stillwellite $LaBGeO_5$," *Kristallografiya*, **37**, 965 – 970 (1992).
3. V. N. Sigaev, E. V. Lopatina, P. D. Sarkisov, et al., "Grain-oriented surface crystallization of lanthanum borosilicate and lanthanum borogermanate glasses," *Mater. Sci. Eng.*, **48**, 254 – 260 (1997).
4. V. N. Sigaev, P. D. Sarkisov, E. V. Lopatina, and S. Yu. Stefanovich, "Polar glass crystal textures based on compounds with stillwellite structure," *Kristallografiya*, **43**, 499 – 504 (1998).
5. V. N. Sigaev, P. D. Sarkisov, P. Bernice, et al., "Surface and bulk stillwellite textures in glasses of the $La_2O_3 – B_2O_3 – GeO_2$ system," *J. Europ. Ceram. Soc.*, **24**, 1063 – 1067 (2004).
6. V. N. Sigaev, "Structure of oxide glasses and formation of polar textures," *Fiz. Khim. Stekla*, **24**, 295 – 307 (1998).
7. V. N. Sigaev, S. Yu. Stefanovich, P. D. Sarkisov, and E. V. Lopatina, "Lanthanum borogermanate glass and crystallization of stillwellite $LaBGeO_5$," *Fiz. Khim. Stekla*, **20**, 582 – 597 (1994).
8. V. N. Sigaev, E. V. Lopatina, P. D. Sarkisov, et al., "Non-isothermal crystallization of $La_2O_3 \cdot B_2O_3 \cdot 2Ge_2O_2$ glasses," *Thermochim. Acta*, **286**, 25 – 31 (1996).
9. V. N. Sigaev, P. D. Sarkisov, and S. Yu. Stefanovich, "Glass crystal texture based on polar phases," *Materialovedenie*, **3**, 35 – 44 (1997).
10. Y. Takahashi, Y. Benino, V. Dimitrov, and T. Komatsu, "Transparent surface crystallized glasses with optical nonlinear $LaBGeO_5$ crystals," *J. Non-Cryst. Solids*, **260**, 155 – 159 (1999).
11. P. Gupta, H. Hain, D. B. Williams, et al., "Structural evolution of $LaBGeO_5$ transparent ferroelectric nano-composites," *J. Non-Cryst. Solids*, **349**, 291 – 298 (2004).
12. Hirokazu Masai, Takumi Fujiwara, Hiroshi Mori, et al., "Dual layered surface crystallization of $30BaO – 15TiO_2 – 55GeO_2$ glass by stepwise heat treatment," *J. Appl. Phys.*, **101**, 79 – 85 (2007).